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IS 6092-3 (1985): Methods of sampling and test for fertilizers, Part 3: Determination of phosphorus [FAD 7: Soil Quality and Gertilizers]



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IS : 6092 (Part 3) - 1985

(Reaffirmed 2001)

Indian Standard

**METHODS OF
SAMPLING AND TEST FOR FERTILIZERS**

PART 3 DETERMINATION OF PHOSPHORUS

(First Revision)

UDC 631.813 : 543.847



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**INDIAN STANDARDS INSTITUTION
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002**

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Indian Standard

METHODS OF SAMPLING AND TEST FOR FERTILIZERS

PART 3 DETERMINATION OF PHOSPHORUS

(*First Revision*)

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**AMENDMENT NO. 1 FEBRUARY 1996
TO
IS 6092 (Part 3) : 1985 METHODS OF SAMPLING
AND TEST FOR FERTILIZERS**

PART 3 DETERMINATION OF PHOSPHORUS

(First Revision)

(Page 13, clause 7.2.2) — Delete.

(PCD 20)

Reprography Unit, BIS, New Delhi, India

Indian Standard
METHODS OF
SAMPLING AND TEST FOR FERTILIZERS
PART 3 DETERMINATION OF PHOSPHORUS
(First Revision)

0. FOREWORD

0.1 This Indian Standard (Part 3) (First Revision) was adopted by the Indian Standards Institution on 5 February 1985, after the draft finalized by the Fertilizers Sectional Committee had been approved by the Petroleum, Coal and Related Products Division Council.

0.2 This standard was first published in 1971. Giving due consideration to the views of manufacturers, testing authorities and the technologists, the concerned Committee decided to revise this standard and felt that the methods of test should be related to those currently used in the industrial laboratories.

0.3 Earlier, only the 'gravimetric quinolinium molybdophosphate method' had been specified for the determination of phosphorus. The present revision includes, as alternatives, 'alkalimetric quinolinium molybdophosphate method' and 'spectrophotometric molybdo-vanado phosphate method' both of which are widely used in laboratories dealing with phosphatic fertilizers. The gravimetric method is, however, to be used as the referee method in case of any dispute.

0.4 In the preparation of this standard, consideration has also been given to the need for maintaining co-ordination with the methods for sampling and test for fertilizers prescribed under the *Fertilizer (Control) Order, 1957* and the *Essential Commodities Act, 1955* (Incorporating amendment up to August 1981), of the Government of India.

0.5 In the preparation of this standard, considerable assistance has been derived from the following publications:

Official methods of analysis. The Association of Official Analytical Chemists, Washington DC, USA. 1978.

Recommended analytical methods. The National Plant Food Institute, Washington DC, USA.

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The Fertilizers and feeding stuff regulations 1960. Department of Agriculture, UK.

0.6 In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960*.

1. SCOPE

1.1 This standard (Part 3) prescribes the methods for determination of phosphorus in its various forms in fertilizers, including fertilizer mixture.

2. SAMPLING

2.1 Representative test samples of the fertilizers shall be prepared as prescribed in IS : 6092(Part 1)-1985†.

3. QUALITY OF REAGENTS

3.1 Unless specified otherwise, pure chemicals and distilled water (see IS : 1070-1977‡) shall be used in tests.

NOTE — ' Pure chemicals ' shall mean chemicals that do not contain impurities which affect the results of analysis.

4. PREPARATION OF SAMPLE FOR ANALYSIS

4.1 Preparation of test sample of the fertilizer shall be done as prescribed in IS : 6092 (Part 1)-1985†.

5. SELECTION OF TEST METHOD AND PREPARATION OF SAMPLE SOLUTION

5.0 General — Methods of determination of total phosphates, water soluble phosphates, citrate soluble phosphates, citrate insoluble phosphates, citric acid soluble phosphates, and free phosphoric acid have been described separately. These methods are applicable to straight as well as mixed phosphatic fertilizers.

*Rules for rounding off numerical values (revised).

†Methods of sampling and tests for fertilizers: Part 1 Sampling (first revision).

‡Specification for water for general laboratory use (second revision).

5.0.1 As stated in 0.3, three methods have been prescribed for determination of phosphorus, namely:

- a) Gravimetric quinolinium molybdophosphate methods,
- b) Alkalimetric quinolinium molybdophosphate method, and
- c) Spectrophotometric molybdovanado phosphate method.

Out of these the first one (gravimetric) shall be the referee method in case of any dispute.

5.1 Preparation of Solution of Sample — Separate procedures for preparing solutions of the samples have been given according to the nature of the sample.

5.1.1 Reagents

5.1.1.1 Concentrated nitric acid — See IS : 264-1976*.

5.1.1.2 Concentrated hydrochloric acid — See IS : 265-1976†.

5.1.1.3 Magnesium nitrate solution — Dissolve 90 g of phosphorus-free magnesium nitrate [$\text{Mg} (\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] in water and dilute to one litre (The material is highly hygroscopic).

5.1.1.4 Concentrated sulphuric acid — See IS : 266-1977‡.

5.1.1.5 Sodium nitrate or potassium nitrate

5.1.1.6 Perchloric acid — 70 to 72 percent.

5.1.2 Procedure

5.1.2.1 Treat 1 g of the prepared sample by the following methods depending on the nature of the sample:

- a) *Suitable for materials containing small quantities of organic matter* — Dissolve in 30 ml of concentrated nitric acid and 5 ml of concentrated hydrochloric acid and boil slowly (in a fume chamber) until organic matter is destroyed.
- b) *Suitable for fertilizers containing large quantities of iron or aluminium phosphate and for basic slag* — Dissolve in 15 to 30 ml of concentrated hydrochloric acid and 3 to 10 ml of concentrated nitric acid and boil till fuming. Cool.

NOTE — For hygroscopic fertilizers, it is preferable to use electric mixer/blender.

*Specification for nitric acid (*second revision*).

†Specification for hydrochloric acid (*second revision*).

‡Specification for sulphuric acid (*second revision*).

- c) *Suitable for organic materials like oil cake, bone meal, fish meal, cotton seed meal along or in mixtures* — Evaporate with 5 ml of magnesium nitrate solution on steam bath, dry thoroughly, ignite to destroy organic matter and dissolve in 1:1 mixture of nitric acid and hydrochloric acid (warm if necessary) when cool, dilute to volume.
- d) *Generally applicable to materials or mixtures containing large quantities of organic matter* — Boil with 20 to 30 ml of concentrated sulphuric acid in a 200 ml long neck flask, adding 2 to 4 g of sodium nitrate or potassium nitrate at the beginning of the digestion and a small quantity of the nitrate after the solution is nearly colourless. When the solution is colourless, cool, add 150 ml of water and boil for a few minutes. Before adding sodium nitrate or potassium nitrate, let the mixture digest, at gentle heat, if necessary, until violence of reaction is over.

NOTE — If the sample contains large amount of calcium, the production of insoluble calcium sulphate in the sulphuric acid digest may create problems, it is better to follow the procedure given in (e).

- e) *Suitable for all fertilizers and mixture containing organic matter* — Boil gently for 30 to 45 min with 20 to 30 ml of concentrated nitric acid in a suitable flask (preferably kjeldahl flask for samples containing large quantities of organic matter) to oxidize all easily oxidizable matter. Repeat with another 20 ml of nitric acid if much organic matter remains. Cool and add 5 to 10 ml of 70 to 72 percent perchloric acid. Boil very gently until solution is colourless or nearly so and white dense fumes appear in the flask. *Do not boil to dryness at any time.* With sample containing large quantities of organic matter, temperature should be raised to fuming point (approximately 170°C) over a period of at least one hour. Cool slightly, add 50 ml of water and boil for a few minutes.

CAUTION — Perchloric acid may cause explosion in contact with organic matter and must not therefore be added unless most of the organic matter is oxidized with boiling nitric acid. Avoid direct contact with perchloric acid. All digestion must be carried out in fume chamber with full proof suction/ventilation device.

Alternatively the sample can be directly digested in 20 to 25 ml of triacid mixture (nitric — perchloric — sulphuric in the ratio of 10:4:2) in 100 to 150 ml kjeldahl flask starting with a low heat till dense fumes of perchloric acid appear. Soluble silica (SiO_2) in the extract interferes with phosphate estimations. In digestion with perchloric/sulphuric acid, it gets dehydrated and becomes insoluble and can be easily filtered off. In hydrochloric acid digest, if soluble silica is expected, this can be dehydrated and thoroughly baked on a sand bath, re-extracted in hydrochloric acid and separated by filtration.

5.1.2.2 Cool the digest obtained in 5.1.2.1, transfer to a 250 ml volumetric flask, dilute to the mark, mix and filter through dry filter discarding the first few ml of the filtrate. Use the filtrate for the tests as specified.

6. TOTAL PHOSPHORUS

6.1 Gravimetric Quinolinium Molydbophosphate Method

6.1.1 Reagents

6.1.1.1 *Citric-molybdic acid reagent* — Dissolve 54 g of pure dry powdered molybdic anhydride (MoO_3) and 12 g of sodium hydroxide (pellets) with stirring in 400 ml of hot water and cool. Dissolve 60 g of citric acid in a mixture of 140 ml of hydrochloric acid and 200 ml of water and cool. Gradually add molybdic solution to citric acid solution with stirring. Cool, filter and dilute to one litre. The solution tends to develop green or blue colour, depending on exposure to light. If necessary, add 0.5 percent solution of potassium bromate drop by drop until green colour becomes quite pale. Store in a dark in a polyethylene bottle.

6.1.1.2 *Quinoline solution* — Dissolve 50 ml of freshly distilled synthetic quinoline with stirring in a mixture of 60 ml of hydrochloric acid and 300 ml of water. Cool, dilute to one litre, and filter. Store in a polyethylene bottle in dark.

6.1.1.3 *Quimociac reagent* — Dissolve 70 g of sodium molybdate dihydrate in 150 ml of water. Dissolve 60 g of citric acid in a mixture of 85 ml of nitric acid and 150 ml of water in a large beaker and cool. Gradually add the molybdate solution to citric acid-nitric acid mixture with stirring. Dissolve 5 ml of synthetic quinoline to a mixture of 35 ml of nitric acid and 100 ml of water. Gradually add this solution to molybdate-citric-nitric acid solution, mix well and let it stand for 24 h. Filter, add 280 ml of acetone, dilute to 1 litre with water and mix well. Store in dark in a corning glass bottle.

6.1.2 Procedure

6.1.2.1 Treat 1 g of the prepared sample as prescribed in 5.1.2.

6.1.2.2 Pipette an aliquot of the filtrate (see 5.1.2.2) containing not more than 25 mg of P_2O_5 into a 500-ml conical flask and dilute to approximately 100 ml with water. Proceed with one of the following methods:

- a) Add 30 ml of citric-molybdic acid reagent and boil gently for 3 min (solution should precipitate free). Remove from heat and swirl carefully. Immediately, add 10 ml of quinoline solution (from a burette) with continuous swirling, first 3 to 4 ml dropwise and then in a steady stream.

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- b) Add 50 ml of quimociac reagent, shake well, cover with watch glass, place on a hot-plate and boil for one minute. The precipitate formed should settle down readily on cooling.

CAUTION — Do not use open flame.

6.1.2.3 Cool to room temperature, swirl carefully 3 to 4 times during cooling, pass through a gooch filter with glass fibre filter paper previously dried at 250°C and weighed, and wash five times with 25 ml portions of water. Alternatively, a good quality G-4 porosity sintered glass crucible (dried at 250°C and weighed) may be used for filtration. Dry the crucible and contents for 30 min at 250°C, cool in a desiccator to constant weight as $(\text{C}_9\text{H}_7\text{N})_3\text{H}_3\text{PO}_4 \cdot 12 \text{ MoO}_3$. Carry out a blank determination with all the reagents without the sample.

6.1.3 Calculation

$$\begin{array}{l} \text{Total phosphates (as } \text{P}_2\text{O}_5 \text{),} \\ \text{percent by mass} \end{array} = \frac{3 \cdot 207 (M_1 - M_2)}{M_3}$$

where

M_1 = mass in g of the residue obtained with the sample,

M_2 = mass in g of the residue obtained in the blank, and

M_3 = mass in g of the prepared sample present in the aliquot taken for the test.

6.2 Spectrophotometric Molybdovanadophosphate Method

6.2.0 General — This method determines ortho-phosphate content of a properly prepared solution. This method is not recommended for materials yielding coloured solution or solution containing ions other than ortho-phosphate which form coloured complex with molybdovanadate. Citrate or excessive amount of chloride interfere by suppressing the colour development.

6.2.1 Apparatus

6.2.1.1 Spectrophotometer — Any commercially available model of proven performance with stray light filter and matched 1-1.5 cm cells. Means for dispelling heat from light source and avoiding voltage fluctuations in the current supply, are to be ensured.

6.2.2 Reagents

6.2.2.1 Molybdovanadate reagent — Dissolve 40 g of ammonium molybdate tetrahydrate in 400 ml of hot water and cool. Dissolve 2 g of ammonium metavanadate in 250 ml of hot water, cool and add 450 ml of perchloric acid (70 percent) or 450 ml of concentrated

nitric acid (Sp Gr 1.42). Gradually add molybdate solution to vanadate solution with constant stirring and when cool, dilute to two litres.

NOTE — Where the sample has already been digested in perchloric acid, nitric acid alone can be used.

6.2.2.2 Standard phosphate solution — Dry pure potassium dihydrogen phosphate (KH_2PO_4) (containing 52.15 percent of P_2O_5) for two hours at 105°C . Cool in a dessicator. Dissolve 0.9588 g of dry potassium dihydrogen phosphate (KH_2PO_4) in distilled water and make up to 500 ml. This contain 1.0 mg $\text{P}_2\text{O}_5/\text{ml}$. Draw out 40, 50, 60, 70, 80 and 90 ml in 100 ml volumetric flask and make up to mark. This will give range of 0.4 to 1.0 mg $\text{P}_2\text{O}_5/\text{ml}$ in increment of 0.1 mg $\text{P}_2\text{O}_5/\text{ml}$. Prepare fresh solutions at intervals of week or 10 days.

6.2.3 Preparation of Standard Curve

6.2.3.1 Pipette 5 ml aliquots of the seven standard phosphate solution (2 to 5 mg P_2O_5) into 100-ml volumetric flasks and add 45 ml of water. Add 20 ml of molybdovanadate reagent by burette or pipette, dilute to volume and make up to mark. Let it stand for 10 min.

6.2.3.2 Select two absorption cells (standard and sample cells) and fill both with the 2 mg P_2O_5 standard. Set spectrophotometer to 400 nm, and adjust to zero absorbance with the standard cell. Sample cell shall also check zero absorbance within 0.001 unit; otherwise read percent absorbance for sample cell and correct subsequent readings. Using sample cell, determine the absorbance of other standard solutions with the instrument adjusted to zero absorbance for 2 mg P_2O_5 standard. After each determination, empty and refill the cell containing 2 mg P_2O_5 standard and readjust zero to avoid error that might arise from temperature changes. Plot absorbance values against concentration (mg P_2O_5 100 ml) of standard solutions. The curve should be as linear as possible.

6.2.4 Preparation of Solution of Sample — Treat 1 g of the prepared sample as in 5.1.2.1(e). Solution should be free from nitrogen oxides and nitrogen oxychloride (as ensured by fuming with perchloric acid). For P_2O_5 content up to 5 percent, dilute to 250 ml. For P_2O_5 content more than 5 percent, dilute to such volume that 5 or 10 ml aliquot contains 3 to 5 mg of P_2O_5 .

6.2.5 Procedure

6.2.5.1 Pipette, into 100 ml volumetric flasks, 5 ml aliquot of standard phosphate solution containing 2 and 3.0 mg $\text{P}_2\text{O}_5/\text{aliquot}$, and develop colour as in 6.2.3.1. Adjust instrument to zero absorbance with 2 mg P_2O_5 standard and determine absorbance of 3.0 mg P_2O_5 standard.

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It is essential that absorbance of latter standard be practically identical with corresponding value on standard curve. It is desirable to carry out the determination with standard and sample solution under the same ambient conditions as temperature has some effect on the intensity of colour developed.

6.2.5.2 *For samples containing up to 5 percent P_2O_5* — Pipette, into a 100 ml volumetric flask, 5 ml of sample solution (6.2.4); and 5 ml of standard phosphate solution containing 2 mg P_2O_5 . Develop colour and determine the absorbance concurrently with and in same manner as for standard phosphate solution given in 6.2.3.1 with instrument adjusted to zero absorbance for 2 mg P_2O_5 standard. Read P_2O_5 concentration from standard curve. With a series of sample solutions, empty and refill cell containing 2 mg P_2O_5 standard after each determination.

6.2.5.3 *For sample containing more than 5 percent P_2O_5* — Pipette 5 to 10 ml of sample solution (6.2.4) into a 100-ml volumetric flask. Without adding standard phosphate solution, proceed as in 6.2.5.2.

6.2.6 Calculation

6.2.6.1 *For samples containing up to 5 percent P_2O_5* —

Total phosphate (as P_2O_5), = $100 \times \frac{[(\text{mg } P_2O_5 \text{ from standard curve} - 2)]}{\text{mg sample in aliquot}}$

6.2.6.2 *For sample containing more than 5 percent P_2O_5* —

Total phosphate (as P_2O_5) = $100 \times \frac{(\text{mg } P_2O_5 \text{ from standard curve})}{\text{mg sample in aliquot}}$

6.3 Volumetric Quinolinium Molybdophosphate Method

6.3.1 Reagents

6.3.1.1 *Quimociac reagent* — conforming to 6.1.1.3.

6.3.1.2 *Standard sodium hydroxide solution* — Dilute 366.32 ml of 1 N sodium hydroxide solution to one litre with CO_2 free water. One millilitre of this solution is equivalent to 1 mg of P_2O_5 .

6.3.1.3 *Standard nitric acid solution* — Prepare nitric acid solution equivalent to molar concentration of standard sodium hydroxide solution and standardize by titrating against it using phenolphthalein. For greater precision use nitric acid solution corresponding to 1/4 or 1/5 of the concentration of standard sodium hydroxide solution.

6.3.1.4 *Citric acid solution* — 10 percent (m/v).

6.3.1.5 Indicators

- a) *Thymol blue* — 0.1 percent. Add 2.2 ml of 0.1 N sodium hydroxide solution to 0.1 g of thymol blue, allow to react for some time and dilute to 100 ml with 50 percent ethyl alcohol.
- b) *Phenolphthalein* — 0.1 percent. Dissolve 0.1 g of phenolphthalein in 100 ml of 50 percent alcohol.
- c) *Mixed indicator* — Mix the three volumes of thymol blue solution and two volumes of phenolphthalein solution.

6.3.2 Procedure

6.3.2.1 Treat 1 g of the sample as given in 5.1.2.

6.3.2.2 Transfer an aliquot of the sample solution containing 20 to 30 mg of P_2O_5 and not more than 5 ml of concentrated acid, to 500-ml conical flask, add 20 ml of 10 percent citric acid solution, and adjust to about 100 ml. Add 60 of quimociac reagent, immediately cover with watch glass, and place on medium temperature hot plate. After the solution comes to boiling point, move to cooler portion of hot plate and boil gently for one minute. Let it cool until flask can be handled comfortably with bare hand. Allow the precipitate to settle down.

6.3.2.3 Prepare a uniform pulped-paper pad about 5 mm thick on perforated porcelain disc in a funnel (60°) fitted on a suction flask by adding not less than 2 approximately equal increments of water suspension of pulped paper and sucking dry with vacuum between additions. Ensure that the setting is leakproof. Swirl the flask, pour contents on to the filter and wash the flask five times with 15 ml portions of water adding washings to funnel. Immediately after funnel has emptied, wash down sides with about 15 ml of water to remove residual acetone, which causes excessively fast drying and later lump formation if allowed to evaporate. Wash with 3 additional 15 ml portions of water, letting funnel empty between additions. Ensure that no free acid is left (precipitate should be washed acid free). Keep drying of precipitate to minimum. Using only a jet of water, transfer the precipitate and pad to precipitation flask and break up the pad with a jet of water. Do not smear the precipitate against the funnel or flask.

6.3.2.4 Dissolve the precipitate by running down standard sodium hydroxide solution in small lots from a burette and add 3 to 5 ml in excess. Add 1 ml of mixed indicator and titrate with standard nitric acid solution to greyish blue end point. If overtitrated (greenish-yellow) add additional excess standard sodium hydroxide solution and re-titrate to greyish-blue.

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6.3.2.5 Blank — Determine a blank on all reagents adding known amount (1 to 2 mg) of P_2O_5 . Use (1 + 9) dilutions of standard sodium hydroxide solution and nitric acid for titration and subtract theoretical titre equivalent to P_2O_5 added from experimental titre. Calculate the difference in volume in terms of 0.366 3 N sodium hydroxide solution and subtract this blank from sample titre.

6.3.3 Calculation

$$\text{Phosphate (as } P_2O_5 \text{), percent by mass} = \frac{(V_1 - V_2 - V_3)}{1\,000} \times \frac{100}{M}$$

where

V_1 = volume in ml of standard sodium hydroxide solution added in 6.3.2.4,

V_2 = volume in ml of standard nitric acid solution added in 6.3.2.4 (adjusted to equivalent concentration of sodium hydroxide solution),

V_3 = volume in ml of standard sodium hydroxide solution in blank determination, and

M = mass in g of the sample present in the aliquot of the sample solution.

7. WATER SOLUBLE PHOSPHORUS

7.0 General — Two techniques for dissolving out the water soluble phosphorus are given in 7.2.1 and 7.2.2. The one given in 7.2.1 is the referee method and that given in 7.2.2 is an alternative one.

7.1 Reagents — In addition to the reagents given in 6.1.1 or 6.2.2 or 6.3.1, the following reagents are required:

- a) Concentrated nitric acid, and
- b) Rectified spirit (or 95 percent ethyl alcohol).

7.2 Extraction of Water Soluble Phosphorus

7.2.1 Place in a funnel 1 g of accurately weighed prepared sample on a 9 cm filter paper in a funnel and wash with small portions of water until the filtrate measures approximately 250 ml. Add freshly distilled water in fine stream directed around entire periphery of filter paper in circular path, ensuring that water and solids are thoroughly mixed with each addition. Let each portion pass through the filter before adding more; use mild suction if washing would not otherwise be complete in about one hour. Ensure complete extraction of P_2O_5 (washing should be free of soluble phosphates). Add 20 to 25 ml of nitric acid to the washings and boil for 15-20 min to hydrolyse non-orthophosphates. Dilute to 250 ml and mix. Preserve the residue for other tests.

7.2.2 Alternative Technique — Place 1 g of the prepared sample in a 500-ml conical flask, wet with 25 ml of rectified spirit and add 225 ml of water. Total volume should be exactly 250 ml. Stopper the flask and fix it to a wrist action shaker. Shake for exactly one hour and filter. If the filtrate is turbid, add a little filter paper pulp and then filter. Reject the first few millilitres of the filtrate before using it for any determination. Preserve the residue for other tests.

7.3 Determination

7.3.1 Gravimetric Quinolinium Molybdophosphate Method — Pipette into a 500-ml conical flask an aliquot containing not more than 25 mg of P_2O_5 . Dilute if necessary to 50 ml. Add 10 ml of nitric acid (1 + 1) and boil gently for 10 minutes. Cool and dilute to 100 ml and proceed as given in 6.1.2.2 and 6.1.2.3.

7.3.2 Volumetric Quinolinium Molybdophosphate Method — Pipette an aliquot containing not less than 30 mg of P_2O_5 in a 500-ml conical flask. Dilute if necessary, to about 50 ml, add 10 ml of nitric acid (1 + 1), and boil gently for 10 min. Cool and dilute to 100 ml and proceed as given in 6.3.2.2 beginning at '.....' add 20 ml citric acid solution.

7.3.3 Spectrophotometric Molybdophosphate Method — conforming to 6.2.

8. CITRATE INSOLUBLE PHOSPHORUS

8.1 Reagents — The following reagents are required in addition to those given under 6.1.

8.1.1 Ammonium Citrate Solution — Dissolve 370 g of crystalline citric acid in 1.5 litres of water and nearly neutralize by adding 345 ml of ammonium hydroxide (28 to 29 percent NH_3). If concentration of ammonia is less than 28 percent add correspondingly larger volumes, and dissolve citric acid in smaller volume of water. Cool and check pH. Adjust with ammonium hydroxide (1 + 7) or citric acid solution to pH 7. Dilute the solution if necessary to specific gravity of 1.09 at 20°C. (The volume will be approximately two litres). Store in tightly stoppered bottles and check pH from time to time. If pH has changed from 7.0, re-adjust.

8.1.2 Ammonium Nitrate Solution — Two or five percent.

8.1.3 Concentrated Hydrochloric Acid — See IS : 265-1976*.

8.2 Procedure

8.2.1 After removing water-soluble phosphorus by the method given in 7.2 transfer the filter and the residue immediately to a 250-ml Erlenmeyer's flask containing 100 ml of ammonium citrate solution

*Specification for hydrochloric acid (second revision).

previously heated to 65°C. Close the flask tightly. Shake vigorously until the paper is reduced to pulp while occasionally relieving pressure by removing the stopper momentarily. Continuously agitate the contents of the stoppered flask in an apparatus equipped to hold the contents of the flask in a thermostatic controlled water bath at 65°C. The arrangement should be such that entire inner surface of the flask and the stopper are continuously bathed with the solution. Exactly 1 hour after adding the filter paper and the residue, remove the flask from the apparatus, and immediately filter the contents by suction as rapidly as possible. Using a filter paper (Whatman No. 5 or equivalent), in a Buchner funnel. Wash with water maintained at 65°C until volume of the filtrate is approximately 350 ml, allowing time for thorough draining before adding more water. If the material yields a cloudy filtrate, wash a few times with 5 percent ammonium nitrate solution.

8.2.2 Determine phosphorus in the citrate insoluble residue by one of the following methods:

- a) Transfer the filter paper and residue, to a porcelain or silica crucible dry and ignite until all organic matter is destroyed. Digest with 10 to 15 ml of concentrated hydrochloric acid and 3 ml of concentrated nitric acid until all phosphates dissolve. Cool and dilute to a known volume.
- b) Treat the wet filter and contents with the method prescribed in 5.1.2.1 (a), (b), (c), (d) or (e). Dilute the solution to 250 ml or other suitable volume, mix well, filter through dry filter paper and determine P_2O_5 as in 6.1 or 6.3. If P_2O_5 present is more than 5 mg (in the aliquot taken for analysis); as in 6.2, if P_2O_5 content is less than 5 mg in the aliquot.

9 AMMONIUM CITRATE SOLUBLE PHOSPHORUS

9.1 Subtract the sum of water-soluble phosphorus and citrate-insoluble phosphorus from total phosphorus to obtain citrate-soluble phosphorus.

10. CITRIC ACID SOLUBLE PHOSPHORUS

10.2 Applicability — This method is not applicable to fertilizers other than basic slag.

10.1 Reagents — In addition to the reagents given under 6.1.1, the following reagents are required.

10.1.1 Citric Acid — monohydrate, crystallized.

10.1.2 Calcium Carbonate — finely ground.

10.1.3 Dilute Sodium Hydroxide Solution — 5 N.

10.1.4 Dilute Hydrochloric Acid — Dilute 250 ml of concentrated hydrochloric acid with water to 1 litre.

10.2 Preparation of Solution — Weigh exactly 5 g of the prepared sample and transfer to a stoppered bottle of about one litre capacity. Separately dissolve 10 g of citric acid in water, dilute to 500 ml and adjust the temperature to 20°C. Add this solution to the sample in the bottle, shaking so as to avoid caking. Shake the bottle continuously in an end on mechanical for exactly 30 minutes. Pour the whole of the liquid at once on to a large medium fine filter and collect the filtrate. If the filtrate is not clear, pass it again through the same filter. Reject first few portions of the filtrate.

10.3 Procedure — Transfer a volume of the solution prepared as in 10.2 containing not more than 25 mg P_2O_5 to a 500-ml conical flask. Dilute the solution with water to 100 ml. If the sample does not contain calcium, add 100 to 200 mg of calcium carbonate. Then add dilute sodium hydroxide solution dropwise until a faint permanent turbidity or precipitate is formed. Dissolve the precipitate by dropwise addition of dilute hydrochloric acid, but avoid an excess. Then proceed with the determination of P_2O_5 by the method prescribed in 6.1, 6.2 and 6.3.

11. FREE PHOSPHORIC ACID

11.1 Reagents

11.1.1 Acetone — 90.5 percent (see IS : 170-1976*).

11.1.2 Standard Sodium Hydroxide Solution — 0.1 N.

11.1.3 Bromo Cresol Green Indicator Solution — Dissolve 0.1 g of bromo cresol green in 100 ml of rectified spirit or ethyl alcohol (95 percent).

11.2 Procedure — Weigh accurately about 2.0 g of the prepared sample into a 250-ml Erlenmeyer flask. Add 100 ml of acetone (check/adjust for neutrality). Fix to a wrist action shaker. Shake for one hour.

11.2.1 Filter through rapid (Whatman No. 4 or equivalent) filter paper into 250-ml Erlenmeyer flask. Wash with four 10 ml portion of acetone. Evaporate acetone as far as possible. Add about 50 ml water and 3 to 4 drops of bromocresol green indicator. Titrate with standard sodium hydroxide solution, until the colour just changes from yellow to blue.

*Specification for acetone (second revision).

IS : 6092 (Part 3) - 1985

11.3 Calculation

$$\begin{array}{l} \text{Free phosphoric acid (as P}_2\text{O}_5, \\ \text{percent by mass} \end{array} = \frac{7.1 \times V \times N}{M}$$

where

V = volume in ml of standard sodium hydroxide solution used,

N = normality of standard sodium hydroxide solution, and

M = mass in g of the prepared sample taken for the test.



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